

Liquid-liquid phase transition model incorporating evidence for ferroelectric state near the lambda-point anomaly in supercooled water.

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We propose a unified model combining the first-order liquid-liquid and the second-order ferroelectric phase transitions models and explaining various features of the λ -point of liquid water within a single theoretical framework. It becomes clear within the proposed model that not only does the long-range dipole-dipole interaction of water molecules yield a large value of dielectric constant ϵ at room temperatures, our analysis shows that the large dipole moment of the water molecules also leads to a ferroelectric phase transition at a temperature close to the λ -point. Our more refined model suggests that the phase transition occurs only in the low density component of the liquid and is the origin of the singularity of the dielectric constant recently observed in experiments with supercooled liquid water at temperature $T \approx 233K$. This combined model agrees well with nearly every available set of experiments and explains most of the well-known and even recently obtained results of MD simulations.

Supercooled water exhibits a number of well-known anomalies near the so-called λ -point at temperature $T_\lambda \approx 228K$ (at normal pressure), where a good number of thermodynamic quantities such as heat capacity, compressibility, thermal expansivity, and dielectric constant all exhibit nearly singular behavior [1–3]. The intrinsic thermodynamic instability of liquid water at temperatures well below the freezing point has been a major obstacle both in experimental studies and theoretical modeling (see e.g. [4–11] for a review). The observed features are often weak, which suggests a thermodynamic continuity of the various water states near the λ -point and relates the observed “singularity” with essentially a random sharp feature, a function of the parameters of the liquid [12, 13]. A considerably more accepted view is to ascribe the features characteristic of a phase-transition to a first-order liquid-liquid phase transition (LLPT). This model predicts the existence of a second critical point of water at the temperature $T_{CR} \sim 200K$ and pressure $\sim 1kbar$ [14, 15]. The sharp temperature dependencies observed near T_λ are attributed to crossing the Widom line [16], where the density and entropy fluctuations are large [17] and which happens at $T \approx T_\lambda$ at normal pressure. The view is supported by numerous molecular dynamics (MD) simulations based on realistic water models [14, 18–26], simplified analytical models [27–31], and experimental studies [4, 32–34]. The reported anomalies are not restricted to static features, the dynamic properties such as the Einstein relation between diffusion and mobility coefficients [35, 36] and the Arrhenius behavior of the liquid’s dynamic properties [16, 36, 37] break down near T_λ as well.

Recent MD studies have demonstrated that heat ca-

capacity and thermal conductivity [38] peak around T_λ as well and that the liquid shows a good deal of ordering in the vicinity of the λ -point. Similarly, recent measurements of the dielectric properties of liquid water confined in nanopores and hence prevented from freezing well below the natural freezing point [39] manifest a profound bump in the dielectric constant near the λ -point [40, 41]. These observations paint a richer picture than a mere first-order liquid-liquid phase transition and, in fact, bring back an old idea [3] relating the weak singularity of the dielectric constant to a ferroelectric phase transition (FPT). Remarkably, the hypothesis was put forward immediately after the discovery of the λ -point, though the weakness of the observed singularities prompted the authors [3] to reject the explanation. Furthermore, the ferroelectric instability for a model liquid with parameters similar to water is predicted to occur at a very high and essentially unreachable temperature, $\sim 1200K$ [42]. A more sophisticated model [43–45] predicts a ferroelectric phase transition at a temperature independent of the details of the short-range interactions between the molecules,

$$T_F = \frac{4\pi n_0 d_0^2}{9\epsilon_\infty} = 210 \div 236K \approx T_\lambda, \quad (1)$$

where n_0 is the density and d_0 are the static dipole moments of the molecule comprising the liquid. The dielectric constant ϵ_∞ is not associated with the molecules’ degrees of orientational freedom and comes from electron shell polarization, $\epsilon_\infty = 4 \div 5.5$ (as discussed in e.g. [46–48]). Despite bringing the phase transition temperature into the right range, the model predicts a behavior of the dielectric constant with changes in temperature that is far too gradual when compared with empirical results [40, 41]. Consequently, it cannot even qualitatively explain all of the features of supercooled water by itself. Realistic liquids such as water are far more complicated

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than a model polar liquid consisting of point dipoles. For example, the tetrahedral geometry of H_2O molecule and its electron shell leads to a polyamorphism phenomenon [4, 7, 49], namely two or more phases of the same liquid existing in a mixture at the same time.

To unify the observed ferroelectric-like properties of water-molecule ordering and the singularity of the dielectric constant near T_λ [40, 41] with the previously reported signatures of the LLPT within a single theoretical framework, we combine our simple polar liquid phenomenology [40, 43–45] with the LLPT hypothesis [4, 14, 15] using a two-component mixture model of water [50]. We assume that the equilibrium state of supercooled water is a mixture of macroscopically-sized clusters of the two types: low density (LDL) and high density liquid (HDL). The LDL local lattice is softer than that of HDL and the density of HDL exceeds that of LDL by $\sim 20\%$ [4, 51–55]. Since LDL is “softer”, the molecules of the LDL rotate more or less freely, whereas in the HDL the rotations are more difficult. This explains why HDL has no ferroelectric state at any temperature. We assume that the ferroelectric ordering and the FPT apparently observed in supercooled liquid bulk water occurs in the LDL component only.

The Gibbs free energy of an LDL cluster at a given pressure P is the sum of the contributions from the polar liquid, G_{LDL}^P , and the lattice, G_{LDL}^L : $G_{LDL} = G_{LDL}^P + G_{LDL}^L$. At high temperatures, $T > T_F$, the equilibrium state of LDL corresponds to the disordered paraelectric phase, whereas at lower temperatures, $T < T_F$, LDL undergoes a second-order phase transition and enters the long-range-ordered ferroelectric state. Near the phase transition, where $\tau = (T - T_F)/T_F \ll 1$, the free energy of LDL takes the form:

$$G_{LDL} \approx -D\tau^2\theta(-\tau) + G_{LDL}^L(T, P), \quad (2)$$

where $D \sim V_0 n_0^2 d_0^2 \sim 150 \text{ cal/mol}$, and $V_0 = N_A/n_0 \approx 22 \text{ cm}^3$ is the molar volume of LDL. Since the LDL density differs by no more than 20% from the total liquid density, we will not distinguish between the LDL density and n_0 . The second-order FPT in LDL manifests itself as a singularity of the dielectric constant ϵ (see e.g. [56]):

$$\epsilon = \epsilon_\infty (1 + f(T)), \quad (3)$$

where $f(T) = 3T_F/(T - T_F)$ at $T > T_F$ and $f(T) = 3T_F/2(T_F - T)$ at $T < T_F$, which is a much weaker dependence than that observed experimentally [40]. The discrepancy is apparently due to the very sharp temperature dependence of the LDL fraction c near $T \approx T_\lambda$. To see that, we follow [50] and formulate a two-liquid model representing the Gibbs energy of water as the energy of a two-liquid mixture of macroscopic clusters using a representation similar to that used in the physics of binary alloys (see e.g. [57]):

$$G(c) = cG_{LDL} + (1 - c)G_{HDL} + Uc(1 - c) + RT[c \log c + (1 - c) \log(1 - c)]. \quad (4)$$

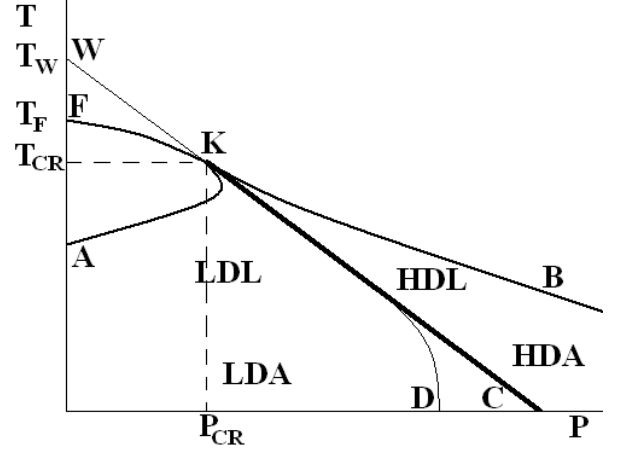


Figure 1: Model PT diagram of water (see the explanations in the text).

Here G_{HDL} is the free energy of the HDL component, and the parameter U characterizes the “energy of mixing”. The equilibrium free energy and the LDL fraction c are found through minimization of $G(c)$ over c , $G'(c) \equiv [\partial G(c, P, T)/\partial c]_{P,T} = 0$, or

$$\Delta G(P, T) + U(1 - 2c) + RT \log \left(\frac{c}{1 - c} \right) = 0, \quad (5)$$

where $\Delta G(P, T) = G_{LDL} - G_{HDL}$. The temperature of the second critical point in the model is $T_{CR} = U/(2R)$ [50].

To analyze these equations, we follow [50, 57] and assume that the thermodynamic quantities in $\Delta G(P, T) = \Delta E^0 - T\Delta S^0 + P\Delta V^0$ are practically temperature-independent:

$$\Delta E^0(P, T), \Delta S^0(P, T), \Delta V^0(P, T) \approx \text{const.} \quad (6)$$

The PT diagram suggested by this model is shown in Fig.1. The AKB line in the Figure is the spinodal line corresponding to $G'(c) = 0$, $G''(c) \equiv [\partial^2 G(c, P, T)/\partial c^2]_{P,T} = 0$. The KB line is the LDL spinodal, where the LDL phase loses its thermodynamic stability (the local minimum of the function $G(c)$ corresponding to the LDL phase disappears on this line). In turn, the KA line is the HDL spinodal. The Gibbs potential $G(c)$ has a single minimum everywhere above the AKB line and two minima below this line, at $c = c_1$ and $c = c_2$. The section KC of the straight line WC is the liquid-liquid first-order phase transition line corresponding to the phase equilibrium conditions: $G(c_1) = G(c_2)$, $G'(c_1) = G'(c_2) = 0$. According to Eqs.(4) and (5), these conditions are equivalent to $\Delta G(P, T) = 0$, which, according to approximation (6), means that T is a linear function of P on the KC line, which means that the KC line is itself a straight line in Figure 1. The low and high density amorphous ice regions are denoted by LDA and HDA.

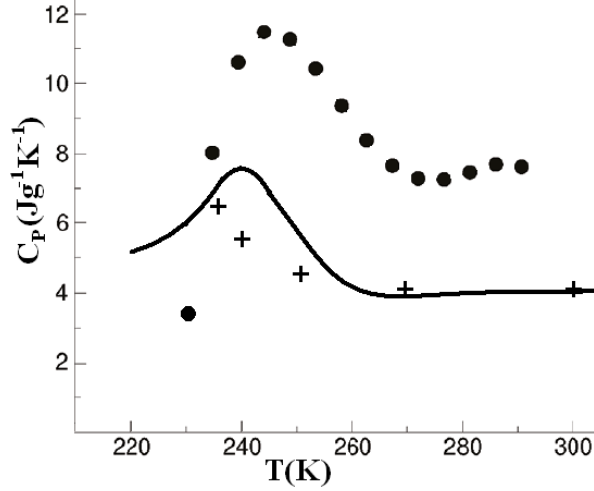


Figure 2: Calculated water heat capacity (formulas (7), (8), (10); solid curve) versus MD calculations [38] (points) and empirical data [1] (crosses).

The KD line in Figure 1 corresponds to the limit $\Delta S \rightarrow 0$ at $T \rightarrow 0$ as required by the third law of thermodynamics and which is never the case under the assumptions (6). WK is the Widom line, defined by the conditions $G'(c) = 0$ and $G'''(c) = 0$, or, equivalently, $c = 1/2$. At small pressures the Widom temperature is $T_W = \Delta E^0 / \Delta S^0$. The heat capacity, C_P , consists of the two parts

$$C_P = T \left[\left(\frac{\partial S}{\partial c} \right)_{P,T} \right]^2 / G''(c) = C_P^P + C_P^L, \quad (7)$$

where C_P^L is the lattice contribution, which can be calculated e.g. using Debye approximation, $C_P^L = C_P^\infty (T/\Theta)^3 / [1 + (T/\Theta)^3]$, where $C_P^\infty = 18 \text{ cal} \cdot \text{mol}^{-1} \text{K}^{-1}$ (as suggested in [1]) and $\Theta \approx 150 \text{ K}$ is the Debye frequency of water. Within the described model the polar part of C_P^P is

$$C_P^P \approx \frac{[\Delta E^0 + P\Delta V^0 + U(1-2c)] [\Delta S^0 - R \log(\frac{c}{1-c})]}{\frac{RT}{c(1-c)} - 2U}. \quad (8)$$

At small pressures along the Widom line $c \approx 1/2$, $G''(c)$ is small, the fluctuations are strong, and the temperature dependence of the heat capacity contribution

$$C_P^P \approx \frac{R\Delta^2}{[(T - T_W)^2 + \delta^2]}, \quad (9)$$

takes a standard Lorenz form, where $\Delta = T_W - T_{CR}$, $\delta = 2R\Delta\sqrt{\Delta/(\Delta E^0 \Delta S^0)}$. The quantity peaks at $T = T_W$ in agreement with experiments [5, 6], earlier explanations [16], and recent calculations [38]. Therefore we can use

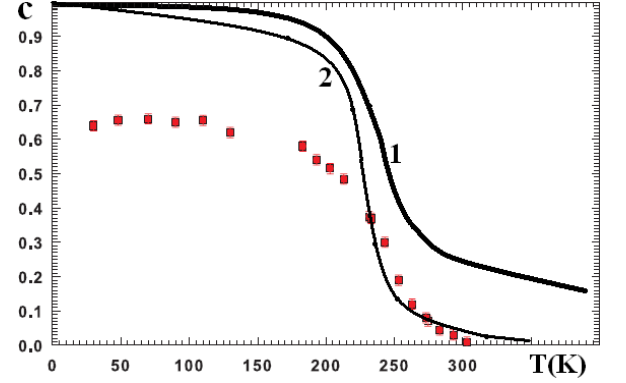


Figure 3: Theoretical temperature dependence of the LDL fraction (solid lines, see the explanations in the text) versus empirical data [33] (dots).

Eq. (9) to analyze the heat capacity calculated e.g. using MD from [38] and extract the model parameters:

$$\Delta E^0 = -860 \text{ cal} \cdot \text{mol}^{-1}, \quad \Delta S^0 = -3.5 \text{ cal} \cdot \text{mol}^{-1} \text{K}^{-1}, \quad (10)$$

and $U = 880 \text{ cal} \cdot \text{mol}^{-1}$. These parameters correspond to $T_W = 245 \text{ K}$, $T_{CR} = 220 \text{ K}$, and $P_{CR} = 1 \text{ kbar}$. To calculate P_{CR} we used $\Delta V^0 \approx 3.8 \text{ cm}^3 \text{mol}^{-1}$ from [50], where very similar parameters were obtained: $U \approx 900 \text{ cal} \cdot \text{mol}^{-1}$, $\Delta E^0 = -250 \text{ cal} \cdot \text{mol}^{-1}$, $\Delta S^0 = -1 \text{ cal} \cdot \text{mol}^{-1} \text{K}^{-1}$, and $T_{CR} = 225 \text{ K}$. These “original” parameters yield smaller critical pressure value: $P_{CR} \approx 0.33 \text{ kbar}$. The heat capacity C_P calculated with the help of Eqs. (7), (8) and (10) is plotted on Fig.2 against the experimental values from [1] and the recent MD calculations [38]. Note that although the MD calculation does not provide a full match with the experimental curve in absolute terms, both data sets consistently describe the same feature and hence apparently the same physics. This in combination with the water molecules ordering predicted by the model (the entropy of LDL is less than that of HDL, $\Delta S^0 < 0$, in accordance with [6]) and confirmed by the MD calculations is the indication of ferroelectric transition implicitly present already in the simulation [38].

Once the model parameters (10) are established we can verify the consistency of the model by observing the temperature dependence of the LDL fraction $c(T)$ given by Eq. (5) (see solid line 1 in Figure 3) and compare it with the empirical data [33] (the dots in the same Figure). There is a qualitative agreement at least at sufficiently large temperatures above 200 K . We note, that $\Delta G(P, T=0) < 0$ as $T \rightarrow 0$ and therefore, at sufficiently low temperatures all of the liquid should turn into LDL, i.e. $c \rightarrow 1$ as $T \rightarrow 0$. This leads us to believe that the equilibrium composition of water was not actually achieved in the experiments of [33], even at very low temperatures. This may well be due to the increase of equilibration time at extremely low temperatures, as discussed in e.g. [58, 59]. With this in mind, we can at-

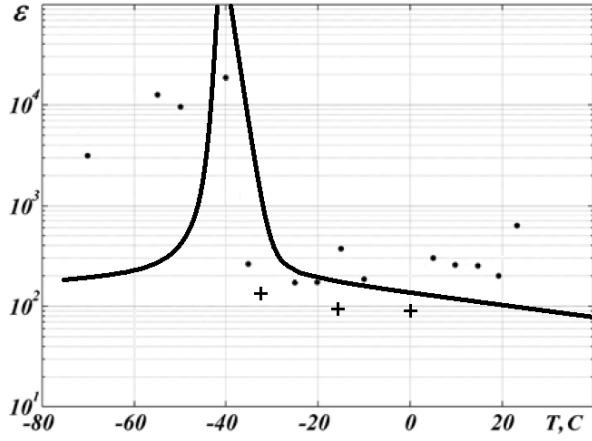


Figure 4: Dielectric constant for bulk water versus temperature. Results of formulas (12), (10) are given by solid curve. Experimental results [40, 41] are presented by points, crosses correspond to the measurements [3].

tempt to match the LDL fraction measurements only at higher temperatures and obtain better agreement with the experiment using slightly different model parameters

$$\Delta E^0 = -920 \text{ cal} \cdot \text{mol}^{-1}, \Delta S^0 = -4 \text{ cal} \cdot \text{mol}^{-1} \text{K}^{-1}, \quad (11)$$

and $U = 900 \text{ cal} \cdot \text{mol}^{-1}$ from [50] (see solid line 2 in Figure 3). Although curves 1 and 2 are clearly different, both sets, (10) and (11), are very close numerically, which indicates further difficulties in refining the parameters due to a very sharp dependence of the LDL fraction c next to the Widom line and clear experimental difficulties.

An analysis of the heat capacity and the LDL fraction measurement let us verify the model and determine the model parameters. Consequently, we may use the model to predict the temperature dependence of the dielectric constant and compare it with empirical data. Accordingly, the dielectric constant of the liquid is the sum of the LDL, $\epsilon_{LDL} = \epsilon_{\infty}(1 + f(T))$ with $f(T)$ from Eq. (3), and the HDL contributions. The HDL fraction is $1 - c$, and its dielectric constant can be described by the Debye-Onsager model [60]: $\epsilon_{HDL} = \epsilon_{\infty} + 2\pi n_0 d_0^2 (\epsilon_{\infty} + 2)^2 / (9T)$. Therefore the full expression $\epsilon = c\epsilon_{LDL} + (1 - c)\epsilon_{HDL}$ becomes

$$\epsilon = \epsilon_{\infty} [1 + c(T) f(\tau)] + [1 - c(T)] \frac{2\pi n_0 d_0^2}{9T} (\epsilon_{\infty} + 2)^2. \quad (12)$$

The predicted temperature dependence calculated using the parameters (10) and the value $\epsilon_{\infty} = 4.7$ corresponding to $T_F = 233 \text{ K}$ is compared with recent experimental measurements [3, 40, 41] in Figure 4. At high temperatures, $T > T_F, T_W$ the model dependence is not far from the experimentally observed values. The temperature dependence is now sharp, much stronger than that predicted by a simpler, single-component model [40]. This

means that including more liquid states in the analysis clearly improves the agreement with experimental results. Below the transition point to the left of the peak, at $T < T_F$, experiments yield distinctly different results. There may be many reasons for that. For example it is quite possible there is more than one LDL state of water below T_F . The temperature T_F itself may depend on the LDL cluster size, and therefore we may face a “continuous set” of ferroelectric transitions in a multitude of LDL forms as the temperature decreases.

When compared with available empirical data and numerical calculations, the model calculations of the heat capacity, LDL fraction, and the dielectric constant support a broader view, implying that supercooled water is indeed a mixture of at least two different components, namely LDL and HDL. There is a growing body of evidence for ferroelectric transition in LDL clusters. Independent of the theoretical arguments given above, the FPT in LDL can be supported by the structural similarity between the local structure of LDL and the crystalline lattice of stable ice Ih [61, 62]. At normal pressure the paraelectric ice Ih enters the ferroelectric state, ice XI, at temperature $T = 72 \text{ K}$ [63–66]. The ferroelectric state, ice XI, is obtained from hexagonal ice Ih after reconstruction of the crystalline lattice, namely, by the shifting of water molecules in each elementary cell of the crystal. It is interesting to note that theory [67] predicts antiferroelectric ordering of molecular dipole moments for Ih ice with undeformed crystalline lattice, but the ferroelectric state with a deformed lattice has a lower free energy. It is not surprising that, due to a less dense local crystalline lattice of LDL, the transition temperature observed in [40, 41] essentially exceeds the corresponding value of FPT “ice Ih \rightleftharpoons ice XI”. It is also worth mentioning here that there have been important studies concerning the ferroelectric states of metastable ice Ic, with a cubic lattice first predicted in [68] and detected experimentally in [69, 70]. The reported explanation of the “ice Ih \rightleftharpoons ice XI” transition gives us cause to believe that the ferroelectric phase transition in LDL is also accompanied by the reconstruction of the local crystalline lattice, i.e. the dipolemoment orientation of molecules is strongly linked to the lattice’s degrees of freedom. On the other hand, FPT occurs only in LDL. Therefore, it is reasonable to assume that the KC line in Figure 1 is in fact the boundary between the ferroelectric and paraelectric regions of the supercooled water. Here $|\Delta G_P| \sim |\Delta G_L|$ and therefore, the molecular orientation and the lattice’s degrees of freedom are equally important “driving forces” of both the ferroelectric and the liquid-liquid phase transitions. Above the FK line the situations is different; there typically $|\tau| \ll 1$ and Eq. (2) yields $|\Delta G_P| \ll |\Delta G_L|$. Therefore, the lattice degrees of freedom dominate. Hence, we believe that supercooled water is ferroelectric below the FKP line.

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